Preparation and characterization edible film packaging from carrageenan

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Abstract. Preparation of edible film from carrageenan has been studied in this research. The edible films were made by phase inversion method with various carrageenan concentrations of 1 %, 1.25 %, 1.5 %, and 1.75 % (b/v) and palm oil as plasticizer with variation concentration of 10%, 20% and 30% (v/v). The edible films were characterized for thickness, tensile strength, elongation, oxygen permeability, water absorption capacity, and solubility. The edible film has been applied for slice apple packaging. The optimize edible films structure were obtained with the carrageenan and palm oil compositions of 1.25% and 10% respectively. The characteristics of the edible films have thickness of 0.23 mm, tensile strength of 102.50 kgf/mm^2, elongation of 7.04%, oxygen permeability of 7.646 x 10-19 cm3.cm/cm^2.s.cmHg. The color brightness test showed significantly different colors at the confidence level of 99.9% and the edible film can prevent 30.7% of weight losses. Edible film can maintain vitamin C of 99,853%.
Key words: edible film, carrageenan, packaging, organoleptic , vitamin C.

Introduction

Packaging of fresh fruits, vegetables, and processed products are indispensable in the effort to maintain the quality of food and agricultural products. It serves as the migration barrier, moisture control, gas, aroma, and other substances of materials into the environment or otherwise. During this time in Indonesia, is still relying on plastic packaging made from petroleum raw materials, such as polystyrene and polyethylene. Petroleum-based plastics are non-biodegradable waste that cause environmental pollution. It is therefore necessary to develop other packaging materials that have superior properties such as plastics that can be reformed biologically (biodegradable) or can even be consumed by humans (edible). This has attracted the interest of researchers to develop a packaging system is a multi-function (Fama *et al*., 2009; Kerry and Butler, 2008). The packaging system is based on the development of edible films using biopolymers (natural polymers) are biodegradable such as polysaccharides, proteins ,fat , or a combination of these compounds. The biopolymer-based films have been widely applied as a protective (barrier) for the transfer of fat, moisture, air ,and smell (taste) for fresh fruits and vegetables, frozen foods, meats , and sweets (Zhong and Xia , 2008; Rizzo and Muratore, 2009)

Edible film is a thin layer of edible, used in food wrapping manner, dipping, brushing, or spraying to provide selective detention against displacement gas, water vapor , and dissolved materials as well as protection against mechanical damage. Theoretically, the material must have properties of edible films resist moisture loss product, has a selective permeability to certain gases, controlling the movement of dissolved solids to maintain the natural color pigments and nutrients, as well as a host of additives like dyes, preservatives and flavor enhancer that improves the quality of foodstuffs (Gennadios and Weller, 1990) .

One of the polysaccharide compounds that can be used as raw material for the manufacture of edible film is carrageenan. Carrageenan can be obtained from seaweed which is one source of cheap raw materials for the manufacture of edible film. Ahmadi *et al.* (2005) prepared edible film of carrageenan with plasticizer sorbitol and palmitic acid. In this study it has not obtained the optimal concentration of carrageenan. Carrageenan concentration are used 0.5 , 0.75 , 1, and 1.25 % (w/v) with plasticizer sorbitol 1 % (v/v) and additives compound palmitic acid with concentrations of 0, 10, 20, 30 % (w/w). Plasticizer is used also very hydrophilic, therefore further research needs to investigate with the variation of carrageenan concentrations above 1.25 % and the use of a more hydrophobic plasticizer in order to get the optimal concentration of carrageenan and alternative plasticizer in the manufacture of edible film .

In this research, an inovation and variation has been done on preparation carrageenan edible film. Plasticizer to be used in this study are palm oil, is expected to increase the hydrophobicity of edible film formed. Edible film preparation begins with the isolation of carrageenan from seaweed flour. Furthermore edible film made by dissolving carrageenan, the addition of plasticizers palm oil, and then printed on the plate support. Formed film was dried and characterized (including tensile strength and elongation, oxygen permeability test, the test water absorption and solubility movie) and applied to the sliced apples .

Materials and Methods

Materials

The materials used were distilled water, methanol, 0.1 N NaOH, $CaCl_2$ 1% (b/v), palm oil, iodine, ethanol.

Extraction and manufacture of carrageenan powder

Red seaweed cut into pieces and soaked in fresh water for 24 hours , then rinsed and drained. Once clean, seaweed boiled in water with sea grass and water ratio of 1 : 15 (w/v), temperature 120 ^{0}C for 15 minutes using a broiler pan. Seaweed was destroyed in a blender and add hot water (90 ^{0}C) with a ratio of 1:30 (w/v). The results are filtered with fine gauze. The filtrate was precipitated by adding methanol with a ratio of 2.5 : 1 (w/v) for 24 hours. Methanol mixed precipitate is filtered with gauze. The filter is still a carrageenan wet, then dried for 4 days. Carrageenan powder obtained after milling process. Carrageenan powder chemically tested qualitatively and characterized by FTIR instrument.

Qualitative test

Carrageenan powder was dissolved in 0.1 N NaOH and added 1 mL $CaCl_2$ (bond formed gelatin). If the gel is formed, showed positive for the presence of carrageenan (Percival and Dowell, 1967) .

Preparation of edible film

Carrageenan powder reconstituted with various concentrations of 1 %, 1.25 %, 1.50 %, and 1.75 % (w/v) in 80 mL of distilled water, and then heated on a hot-plate stirrer until it reaches a temperature of 70 ^oC. Furthermore palm oil added 1 % (v/v) and distilled water to a total volume of 100 mL. After it is heated again to a temperature of 85 °C for 5 min. Printing is done by pouring 100 mL of solution in the plate measuring 25x16x2 cm. Drying is done by using an oven at a temperature of 50 °C for 18-24 hours. Edible film obtained from the plate removed and stored in a desiccator. Edible films produced were characterized for tensile strength and tensile strength of edible films with the best selected and used to study the effect of plasticizer concentration of palm oil. Making edible film with variation of palm oil was the same as the above experiment in which the addition of palm oil with concentrations varied as follows : 0 %, 10 %, 20 % and 30 % (v/w carrageenan). All produced edible characterized including film thickness, tensile strength, oxygen permeability test, water absorption and solubility.

Tensile strength test

Tensile strength was measured using Autograph (Shimadzu, Japan). The method used is ASTM Method D-882. Previous edible films conditioned in room temperature of 25 °C and 75 % RH for 72 hours. For tensile strength, the test was done by the paired sample grip the top and bottom. Values on the recorder (recorder) is clear test is started by pressing the UP button. Press the STOP button just as edible film samples broke. Press RETURN to restore grip to its original position. The sample size used for this test is 7 x 3.5 cm (70 mm x 35 mm) with a tensile speed = 700 mm / min, grip weight = 50 N / 5 Kgf , extensive sample (A) = (70 x35) mm^2. Tensile strength (kgf/mm^2) = Value tensile samples /sample area. Percent elongation values can be read on Autograph. Sample extension automatically available in the form of an extension of the film difference (ΔL, mm).

Oxygen permeability test

Oxygen permeability characteristics measured by ASTM method D-3985 (ASTM 1992). Film sample measuring 4 x 4 cm with a thickness ranging from 0.6 to 2.8 mm (depending on the coating film is formed by the concentration difference of materials) prepared with water content of 2.5 %. Permeability tester tool used tubular and fitted pressure gauge and a temperature controller. Samples are placed in the center of the tube. Measurements were performed at room temperature using oxygen gas as a flow tester on one side of the tube. Pressure loss is proportional to the amount of oxygen that diffuses through the film .

Water absorption and solubility Test

The water absorption test performed with modified ASTM standard D570- 81 test method. Film sample was dried in an oven at a temperature of 40 ^{o}C for 24 hours, then cooled in a desiccator and weighed. Film soaked with distilled water in a petri dish marinated for 24 hours. After immersion, the film is dried with paper towel and weighed again. To calculate the weight loss, the film was dried in an oven for 24 hours. After drying, the samples were placed in a desiccator and weighed. Weight difference of the initial weight is weight loss or solubility of edible film.

Organoleptic

Organoleptic tests carried out by way of sensory observations (eye) by 15 panelists on sliced apples in the apple slices wrapped and unwrapped. The test performed by assessing the suitability or color difference between apple slices wrapped and unwrapped.

Shrinkage test

Test weight shrinkage sliced apples is done by calculating the difference in initial weight and weight of apple slices after five days of storage .

Determination of vitamin C

Sliced apples weighed 100-150 g, blend until a slurry. Then weighed 5 g slurry and put in 100 ml flask and added distilled water to mark boundaries then filtered and the filtrate obtained vitamin C. Then 20 mL of the filtrate was taken and put in a 125 mL erlemeyer and added 2 mL of 1% starch. And then titrated with a standard solution of 0.01 N iodine, and calculated levels of vitamin C. 1 mL of iodine 0.01 N = 0.88 mg of vitamin C.

Results and Discussion

Isolation and purification of Carrageenan

Seaweed first cut, washed and soaked in fresh water for 24 hours to remove salt and impurities that may be attached to the storage period. Seaweeds have clean subsequently extracted using water as much as 40-50 times the weight of dried seaweed, by boiling for 15 minutes. Boiling is intended to facilitate the extraction of carrageenan when crushed in a blende. Soft seaweed blend using hot water extraction of polysaccharides to complete and accelerate the elimination of 6-sulfate of monomer units to 3.6 -anhidro- D-galactose, thus increasing the gel strength (Winarno, 1996). Separation of extracts and residues (impurities consisting of seaweed that does not dissolve) performed by filtration using filter cloth in hot conditions to avoid the formation of gel. Extract obtained was precipitated by adding methanol to obtain carrageenan. The resulting wet carrageenan dried to obtain dry carrageenan, then blended into a flour. Carrageenan powder obtained has not been established purely because there is still the possibility of other compounds such as agar, alginates, proteins and fats. Yield carrageenan obtained was 57.5 % (from 800 grams of weight gained dried seaweed carrageenan powder 460 grams dry weight). Theoretically yield carrageenan contained in the red seaweed is 54-73 % (Atmadja, 1996).

Qualitative analysis of carrageenan is prove a positive results by the formation of a gel. Gel formation due to carrageenan is sensitive to potassium ions and form a strong gel in the presence of potassium salts (Glicksman, 1983). Carrageenan powder were analyzed by infrared spectroscopy shown in Figure 1. Carrageenan FTIR spectrum showed a wide absorption at wavenumber 3423.4 cm^{-1} for the hydroxyl group (OH) and group NH (amine), a characteristic of carrageenan compound. Obtained FTIR spectra when compared with the standard carrageenan FTIR spectrum shows a very similar spectrum.

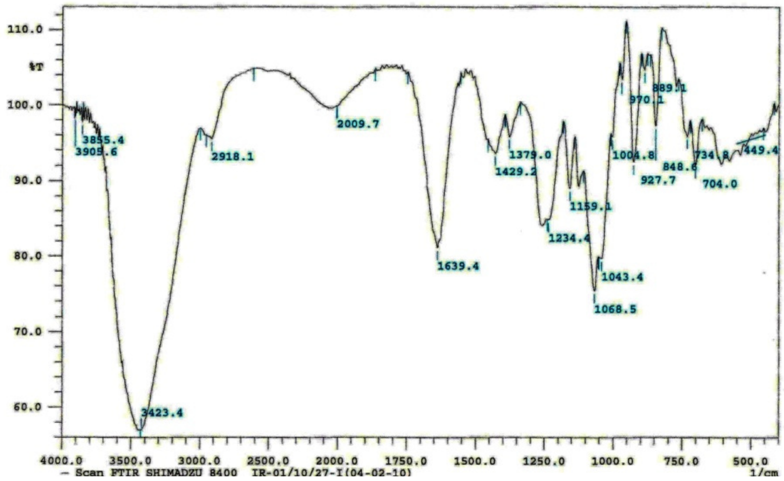

Figure 1. Spectrum FTIR of powder carregeenan

Tensile Strength of Edible Film

The results of tensile strength and elongation of the edible film with variation of carrageenan concentration can be seen in Table 1. From the tensile test results in Table 1 it can be seen that the highest tensile strength of edible films edible film obtained at a concentration of 1.25 % carrageenan. At a concentration of 1.5 % tensile strength values back down. At a concentration of 1.75 % carrageenan powder is not got the result, is apparently due to the higher concentration of carrageenan were added to increase the strength of inter-chain molecules in the matrix edible film, so that the resulting edible film more brittle and stiff. This causes a decrease in the ability of elongated edible film when subjected to force, edible films become brittle and easily broken (Ahmadi *et al.*, 2005). Highest elongation value obtained in the edible film with a concentration of 1.5 % carrageenan powder. Meilina *et al.* (2006) reported in their publications tensile edible coating of pectin ranged between 18.492-33.533 kgf/mm^2. Indarti *et al.* (2006) reported a tensile test of edible film sago ranged from 38.776 to 43.700 kgf/mm^2. Haris (2001) reported a tensile test tapioca starch edible film of 6.97 kgf/mm^2. Based on the test results of tensile strength and elongation, edible film with a concentration of 1.25 % carrageenan flour deserves to be tested further, because it has the tensile strength and elongation are worthy to serve as an edible film.

Table 1. Tensile strength and elongation of edible films with various concentrations of carrageenan

Edible film with variation carrageenan content	Tensile Strength (Kgf/mm2)	Elongation (%)
1 % (w/v)	51,67	3,84
1,25 % (w/v)	102,50	7,04
1,5 % (w/v)	83,33	7,15

Oxygen Permeability Test

Permeability is the ability to skip the film of oxygen gas in a unit area of material in certain circumstances. Permeability value is strongly influenced by the chemical nature and structure of the polymer. Oxygen permeability values on packaging films useful for estimating the shelf life of packaged products.

Table 2. Oxygen permeability of edible film carrageenan

Edible Film with difference palm oil content (%)	Permeability Oxygen (cm3.cm/cm2.s.cmHg)
10	7,646 x 10-9
20	8,245 x 10-9
30	7,925 x 10-9
40	8,316 x 10-9

Table 2 shows that the highest oxygen permeability values obtained in 4 samples with additing 40% palm oil. High oxygen permeability of edible films showed resistance to low oxygen permeability. Vice versa, the value of the low permeability of edible films showed resistance to high oxygen permeability. Edible films made are expected to have a low permeability value as edible films will be applied to wrap the apple slices. Suitable edible film used to wrap slices of apple fruit is edible film with the addition of 10% palm oil. Edible films with low oxygen permeability value is suitable for wrapping sliced apples for apple slices are sensitive to oxygen which causes browning in apples.The addition of palm oil causes rise in the value of the oxygen permeability of edible film carrageenan. This is thought to occur due to palm oil reduce the density of edible film that carrageenan increased oxygen permeability values.

Water Absorption and Solubility of Edible Films

The test results showed that the solubility of edible film of carrageenan edible film has a very large solubility, so the piece as a whole edible film dissolves in less than 2 hours. Solubility of the edible film because of the hydrophilic nature. The great solubility causes the absorption of water could not be determined. Krotcha *et al.* (1994) reported that the edible film of hydrocolloids (carrageenan) has resistance to water vapor is very low but has good resistance to gases O_2, CO_2 and fat.

Applications of Edible Films

Results of organoleptic test for the color brightness apple slices in 5 days by 14 panelists are shown in Table 3. The table shows that the second day since the storage, apple slices wrapped in edible film showed significantly different colors on a 99.9% confidence level compare to unwrapped apple slices. Apple slices wrapped with edible film is not dark and moldy. If the number panelist involved 14 persons, for a confidence level of 99.9% or 0.1% error rate there must be 13 panelist confirmed different color.

Table 3. Results of the organoleptic apple slices

Days	Number of Panelist	Number of Differences
1	14	0
2	14	13
3	14	14
4	14	14
5	14	14

Shrinkage test wrapped slices of edible film with the addition of palm oil 10% indicated that the resulting edible film can prevent severe shrinkage of the apple. On samples wrapped in heavy shrinkage occurs at 47.4%, whereas in the control (non-wrapped apples) occurs severe shrinkage of 78.1%. This suggests that the resulting edible film can prevent severe shrinkage sliced apples by 30.7% compared with that without the wrapped apples.

Vitamin C or ascorbic acid has a molecular weight of 178 with a molecular formula $C_6H_8O_6$. Vitamin C levels are determinated base on the principle of oxidation-reduction by using titration or titration Iodimetri directly. In this case iodine is I_2 or titrant. I_2 is an oxidator that is not too strong so that only substances which are fairly strong reducing agent that can be titrated. Indicator used is starch with color change from colorless to blue. The results showed levels of vitamin C fresh apple slices at 0.375% while the vitamin C content of apple slices wrapped with edible films and stored for 5 days gave 0.228%. Difference in levels of vitamin C before and after the acquired wrapped by 0.147%. This indicates that the edible film carrageenan can prevent decreased levels of vitamin C sliced apples.

Conclusions

The Isolation product of carrageenan from seaweed obtained for 57.6 % (w/w). Carrageenan edible film has casted at the composition of 1.25 % carrageenan has a tensile strength and elongation 102.50 kgf/mm^2 and 7.04 % respectively. Palm oil may increase the hydrophobic properties of edible film but at high concentrations can reduce the resilience of edible film to oxygen gas. The optimize edible films structure were obtained with the carrageenan and palm oil compositions of 1.25% and 10% respectively. The characteristics of the edible films have thickness of 0.23 mm, tensile strength of 102.50 kgf/mm2, elongation of 7.04%, oxygen permeability of 7.646 x 10^{-19} cm^3.cm/cm^2.s.cmHg. The color brightness test showed significantly different colors at the confidence level of 99.9% and the edible film can prevent 30.7% of weight losses. Edible film can maintain vitamin C of 99,853% or can prevent reduction of vitamin by 0.147%. Carragenan edible film can be an alternative packaging material for foods and vegetables.

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References

Ahmadi, dan Anggrahini 2005. Ekstraksi Karagenan Eucheuma cottonii dari Perairan Nusa Dua Bali dan Pemanfaatannya Sebagai Edible Film. Program Ilmu Studi dan Teknologi Pangan Pasca Sarjana UGM. Yogyakarta

ASTM, 1988. Annual Book of ASTM Standards American Society for Testing and Materials, Philadelphia.

Atmadja, 1996, Pengenalan Jenis-jenis Rumput Laut Indonesia, Puslitbang Oseonologi LIPI, Jakarta.

Famá, L., L. Gerschenson, and S. Goyanes, 2009, Starch-vegetable fibre composites to protect food products, Carbohydrate Polymers, 75(2), p. 230

Gennadios,A. dan C.L. Weller, 1990. Edible Film and Coatings from Wheat and Corn Proteins. J. Food Tech. 44(10):63-68.

Gliksman, M., 1983. Food Hydrocolloids, Volume 1, CRC Press, Florida.

Haris, H., 2001. Kemungkinan Penggunaan Edible Film dari Tepung Tapioka Untuk Pengemasan Lempuk, Laporan Penelitian, Fakultas Pertanian, Universitas Bengkulu, Bengkulu.

Indarti, E.; Fahrizal (2006). Kajian Pengaruh Konsentrasi dan Jenis Plasticizer Terh adap Kekuatan Fisik Edible Film dari Sagu, Laporan Penelitian, Universitas Syiah Kuala, Banda Aceh.

Krotcha, J. M., E. A. Baldwin, dan M. O. N. Carriedo, 1994. Edible Coatings And Films to Improve Food Quality. Technomic Publishing, Co., Lancaster.

Percival dan Mc. Dowell, 1967. Chemistry and Enzymology of Marine Algae Polysacharides, Academic Press, London and New York.

Rizzo, V. and G. Muratore, 2009, Effects of packaging on shelf life of fresh celery, Journal of Food Engineering, 90(1), p. 124

Siracusa, V., et al.., 2008, Biodegradable polymers for food packaging: a review, Trends in Food Science & Technology, 19(12), p. 634

Winarno F.G., 1996, Teknologi Pengolahan Rumput Laut, Pustaka Sinar Harapan, Jakarta.

Zhong, Q.P. and Wen-Shui Xia, 2008, Physicochemical Properties of Edible and Preservative Films from Chitosan/Cassava Starch/Gelatin Blend Plasticized with Glycerol Food Technol. Biotechnol. 46 (3) 262–269